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The present research effort developed a real-space formulation for orbital-free density functional theory and Kohn-Sham density functional theory in order to conduct large-scale electronic structure calculations that take an important step towards addressing the prevailing domain-size and geometry limitations of existing electronic-structure codes. In particular, by combining the real-space formulation with a finite-element discretization, which has the desirable attributes of a local basis that is amenable to coarse-graining and a scalable

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ABSTRACT

The present research effort developed a real-space formulation for orbital-free density functional theory and Kohn-Sham density functional theory in order to conduct large-scale electronic structure calculations that take an important step towards addressing the prevailing domain-size and geometry limitations of existing electronic-structure codes. In particular, by combining the real-space formulation with a finite-element discretization, which has the desirable attributes of a local basis that is amenable to coarse-graining and a scalable discretization on parallel-computing platforms, it has been demonstrated that large-scale electronic structure calculations at macroscopic scales become accessible to conduct an accurate electronic structure study of the energetics of defects in materials. Careful verification and validation studies of the developed techniques and codes for both orbital-free DFT and Kohn-Sham DFT have been conducted. Using orbital-free DFT the energetics of vacancies in Aluminum as well as the properties of Al-Mg alloys have been investigated. Using Kohn-Sham DFT the studies on the energetics of Ni-Al bi-layers are ongoing. The present research study was conducted in close collaboration with scientists at Army Research Labs. In this report we provide a summary of our research accomplishments and comment on our ongoing and future work.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>   <u>Paper</u>

08/07/2012   3.00 Phani Motamarri, Mrinal Iyer, Jaroslaw Knap, Vikram Gavini. Higher-order adaptive finite-element methods for orbital-free density functional theory,
Journal of Computational Physics, (8 2012): 0. doi: 10.1016/j.jcp.2012.04.036

08/07/2012   5.00 Balachandran Radhakrishnan, Vikram Gavini. Effect of cell size on the energetics of vacancies in aluminum studied via orbital-free density functional theory,
Physical Review B, (9 2010): 0. doi: 10.1103/PhysRevB.82.094117

08/07/2012   4.00 Vikram Gavini, Liping Liu. A homogenization analysis of the field theoretic approach to the quasi-continuum method,
Journal of the Mechanics and Physics of Solids, (8 2011): 0. doi: 10.1016/j.jmps.2011.04.020

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<u>Received</u>   <u>Paper</u>

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B. G. Radhakrishnan, V. Gavini, Electronic structure calculations at macroscopic scales using orbital-free DFT, ASME International Mechanical Engineering Congress and Exposition, Vancouver, Nov 11-17, 2010.

B. G. Radhakrishnan, V. Gavini, Electronic structure calculations at macroscopic scales using orbital-free DFT, SIAM meeting on Mathematical aspects of Materials Science, Philadelphia, PA, May 23-26, 2010.

B. G. Radhakrishnan, V. Gavini, Electronic structure calculations at macroscopic scales using orbital-free DFT, American Physical Society Meeting, Portland, OR, March 15-19 2010.

B. G. Radhakrishnan, V. Gavini, Quantum Mechanics to Mechanics: Electronic structure calculations at macroscopic scales, 10th U.S. National Congress on Computational Mechanics, Columbus, OH, July 16-19, 2009.

Number of Presentations: 4.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

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(d) Manuscripts

Received	Paper
07/12/2011	1.00 Gavini V., Liu L., . Effect of cell size on the energetics of vacancies in aluminum studied via orbital-free density functional theory, (09 2010)
07/12/2011	2.00 Gavini V., Liu L.. An analysis of the field theoretical approach to the quasi-continuum method, Journal of Mechanics Physics Solids (07 2011)
08/08/2012	6.00 Phani Motamarri, Michael R. Nowak, Kenneth Leiter, Jaroslaw Knap, Vikram Gavini. Higher-order adaptive finite-element methods for Kohn-Sham density functional theory, Journal of Computational Physics (06 2012)

TOTAL: **3**

Number of Manuscripts:

Books

Received	Paper

TOTAL:

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Patents Awarded

Awards

Young Investigator Award, Air Force Office of Scientific Research, 2013

Humboldt Research Fellowship (Experienced Researcher), Alexander von Humboldt Foundation, 2012

CAREER Award, National Science Foundation, 2011

Graduate Students

NAME	PERCENT SUPPORTED	Discipline
Mrinal Iyer	0.75	
Balachandran Radhakrishnan	0.25	
Phani Motamarri	0.20	
Janakiraman Balachandran	0.33	
FTE Equivalent:	**1.53**	
Total Number:	**4**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Vikram Gavini	0.12	
FTE Equivalent:	**0.12**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Michael Nowak	0.20	Electrical Engineering and Computer Science
FTE Equivalent:	**0.20**	
Total Number:	**1**	

Student Metrics
This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Mrinal Iyer
Total Number: **1**

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

<center>

Final Report

Electronic Structure Calculations on Reactive Nano-films

</center>

<center>

Principal Investigator:
Vikram Gavini
Department of Mechanical Engineering
University of Michigan, Ann Arbor

Program Manager:
Dr. Dave M. Stepp
Materials Science Division
Army Research Office

</center>

Abstract

The present research effort developed a real-space formulation for orbital-free density functional theory and Kohn-Sham density functional theory in order to conduct large-scale electronic structure calculations that take an important step towards addressing the prevailing domain-size and geometry limitations of existing electronic-structure codes. In particular, by combining the real-space formulation with a finite-element discretization, which has the desirable attributes of a local basis that is amenable to coarse-graining and a scalable discretization on parallel-computing platforms, it has been demonstrated that large-scale electronic structure calculations at macroscopic scales become accessible to conduct an accurate electronic structure study of the energetics of defects in materials. Careful verification and validation studies of the developed techniques and codes for both orbital-free DFT and Kohn-Sham DFT have been conducted. Using orbital-free DFT the energetics of vacancies in Aluminum as well as the properties of Al-Mg alloys have been investigated. Using Kohn-Sham DFT the studies on the energetics of Ni-Al bi-layers are ongoing. The present research study was conducted in close collaboration with scientists at Army Research Labs. In this report we provide a summary of our research accomplishments and comment on our ongoing and future work.

1 Orbital-free Density Functional Theory:

Orbital-free density functional theory is an approximation to Kohn-Sham density functional theory–which is widely accepted as a reliable and computationally tractable materials theory–where the kinetic energy of non-interacting electrons is explicitly modeled as a functional of the electron density. The development of model kinetic energy functionals for orbital-free DFT is an active area of research, and the model kinetic energy functionals developed over the past decade seek to capture the known properties of uniform electron gas (Wang & Teter, 1992; Wang et al., 1998, 1999), and numerical investigations have demonstrated the accuracy of these kinetic energy functionals for materials systems whose electronic structure is close to a free-electron gas. For these materials systems, orbital-free DFT provides a computationally efficient approach of computing material properties owing

<center>1</center>

to the linear-scaling of its computational complexity with systems size (as opposed to a cubic scaling for conventional Kohn-Sham DFT implementations). The main aspects of the proposed algorithmic developments in orbital-free DFT include:

(i) **Real-space formulation:** The ground-state energy of a materials system described by DFT is given by:

$$E(\rho, \boldsymbol{R}) = T_s(\rho) + E_{xc}(\rho) + E_H(\rho) + E_{ext}(\rho, \boldsymbol{R}) + E_{zz}(\boldsymbol{R}) \tag{1}$$

where ρ denotes the electron-density, $\boldsymbol{R}$ denotes the positions of nuclei, T_s is the kinetic energy of non-interacting electrons, E_{xc} denotes the exchange-correlation energy, E_H denotes the Hartee energy involving the Coulomb interaction between electrons, E_{ext} denotes the electrostatic interaction between electrons and ions, and E_{zz} is the nuclear-nuclear repulsion energy. In the present effort, we restricted ourselves to LDA exchange-correlation functionals, and developed the formulation for the Thomas-Fermi-Weizsacker family of orbital-free kinetic energy functionals as well as the Wang-Govind-Carter (WGC) kinetic energy functionals which involves a non-local kernel energy. The various terms in the energy functional are local, excepting the electrostatic interaction and the kernel energies that are extended in the real-space. In seeking a local real-space formulation, which is an important aspect of the subsequently developed coarse-graining schemes, we developed a local variational reformulation of the extended interaction. In particular, the extended electrostatic interactions have been reformulated by taking recourse to the solution of a Poisson's equations. Further, the non-local kernel energies have been reformulated into a local variational formulation by solving a coupled system of Helmholtz equations. The details and the associated mathematical properties of our local reformulation are discussed in our published manuscripts Radhakrishnan & Gavini (2010); Motamarri et al. (2012).

(ii) **Finite-element discretization:** A general finite-element (FE) framework has been developed for the discretization of orbital-free DFT as well as the subsequently discussed Kohn-Sham DFT. In particular, the developed framework supports higher-order finite-elements up to 8th order, including spectral finite-elements which are better conditioned for higher-order discertizations, ability to generate coarse-grained discretizations with robust meshing scripts for CUBIT, domain decomposition in parallel using PARMETIS. As part of this research effort, we investigated the computational efficiency afforded by higher-order finite-element discretizations. In particular, we investigated the convergence rates for the various order of finite-element approximations and the computational efficiency afforded by using higher-order discretization. We found close to optimal rates of convergence for the discretization errors despite the non-linear nature of the energy functional (cf. Figure 1). Further, for accuracies commensurate with chemical accuracy, we found significant computational advantage by using higher-order basis over linear FE basis. In particular, the computational advantage was over 100-fold for the fourth-order FE basis over linear FE basis (cf. Figure 2), with diminishing returns beyond fourth-sixth order.

(iii) **Solution strategies:** In order to solve the non-linear coupled system of equations describing the electron-density, electrostatic potential and the kernel potentials (c.f Motamarri et al. (2012) for the formulation), two strategies have been explored: (i) A *staggered solve* where for any change in electron-density the electrostatic potential are recomputed;
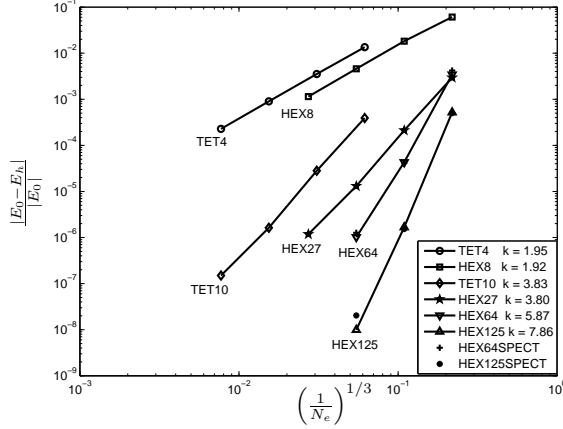
Figure 1: Convergence rates for the finite-element approximation of bulk Aluminum using orbital-free DFT with DD kernel energy. (Motamarri et al., 2012)
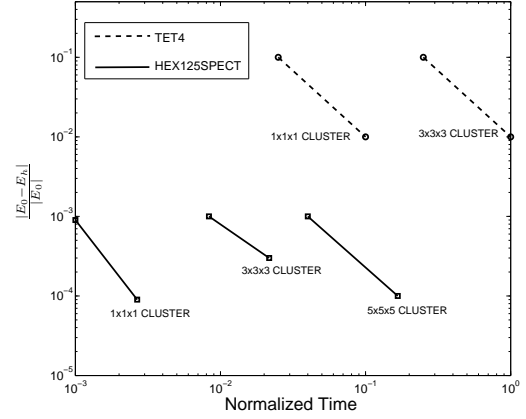

Figure 2: Computational efficiency of various orders of finite-element approximations. Case study: Aluminum clusters of varying sizes. (Motamarri et al., 2012)

(ii) A *simultaneous solve* where all the coupled systems of equations are solved simultaneously. Our mathematical analysis shows that the staggered solve is the most robust (Motamarri et al., 2012), though it is computationally also expensive. Our numerical studies suggest that the robustness of the simultaneous solution of electron-density and electrostatic potential can be significantly improved by using improved preconditioners like block-Jacobi. The various aspects of the developed solution strategies are discussed in our published manuscript Motamarri et al. (2012).

(iv) **Coarse-graining using quasi-continuum reduction:** Building on the ideas proposed in Gavini et al. (2007) the quasi-continuum (QC) reduction for orbital-free DFT with WGC kinetic energy functionals was developed. The main ideas constituting the development of this coarse-graining technique, which made possible orbital-free DFT based electronic structure calculations on multi-million atom system, constitute: (i) the aforementioned local variational reformulation of the orbital-free DFT ground-state energy; (ii) an effective use of the coarse-graining ability of finite-element basis by providing higher-resolution where necessary—e.g. near the defect-cores—and coarse-graining elsewhere. Details of the method are discussed in Gavini et al. (2007) for TFW kinetic energy functionals and its extension to account for WGC kinetic energy functionals, developed in part during this research effort, is discussed in Radhakrishnan & Gavini (2010). The developed QC reduction was used to study the cell-size effects in the formation energies of vacancies and di-vacancies. It was found that, even for simple defects like vacancies, the cell-size effects can be significant up to 1000 atoms. Our studies suggest that the elastic fields, as well as, the perturbations in electronic fields produced by defects are long-ranged, and that cell-sizes larger than those used conventionally may be necessary to accurately compute the energetics of defects. Figure 3 shows the cell-size dependence of the mono-vacancy formation energy.

(v) **Transferability studies on orbital-free kinetic energy functionals for Al-Mg alloys:** As part of the present effort, a study was also conducted to validate the transferability of the orbital-free WGC kinetic energy functional to predicting properties of
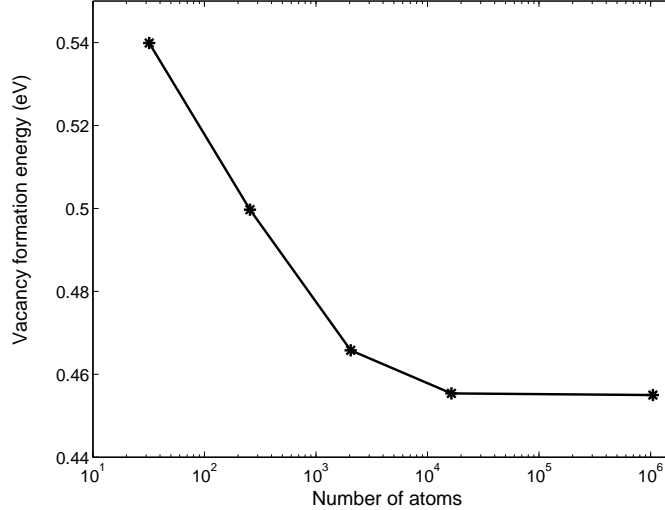
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Figure 3: Cell-size study of mono-vacancy formation energy. (Radhakrishnan & Gavini, 2010)

Al-Mg alloys—a material system of significant interest in developing light-weight materials for transportation. In particular, we studied the phase stability of these alloys, and the results are presented in the table below. The β' alloy has 879 sites in the unit cell with a disorder in 20 of these sites. In our studies we considered the two extreme cases of all the 20 sites to be either occupied by Al (denoted as $\beta'(Al)$) or by Mg (denoted as $\beta'(Mg)$). These studies show that the orbital-free kinetic energy functionals can predict the relative stability of the various phases accurately, which is a stringent validation test. Further, these studies also demonstrate the efficiency of the developed algorithms which allow the consideration of large cell-sizes—for instance the β' alloy containing 879 sites.

Table 1: Formation energies of the various Al-Mg alloys computed using WGC orbital-free kinetic energy functionals using bulk local pseudopotentials (Zhou et al., 2004). Kohn-Sham DFT calculations using ABINIT with Troullier-Martins pseudopotential are used as the validation benchmark. All the energies reported are in $eV/atom$, and negative formation energy denotes an energetically favorable alloy formation. Kohn-Sham DFT calculations for the β' alloy could not be conducted due to the large system size.

Alloy	Al_3Mg	$Al_{14}Mg_{13}$	$Al_{12}Mg_{17}$	$Al_{30}Mg_{23}$	$\beta'(Al)$	$\beta'(Mg)$
Orbital-free DFT	-0.013	0.069	-0.007	-0.001	-0.026	-0.084
Kohn-Sham DFT	-0.009	0.062	-0.02	-0.016	NA	NA

2   Kohn-Sham Density Functional Theory:

While orbital-free DFT is attractive due to the linear-scaling complexity in system size, the accuracy of the kinetic energy functionals limits the consideration of materials systems to those whose electronic structure is close to free-electron gas. Thus, as part of this research
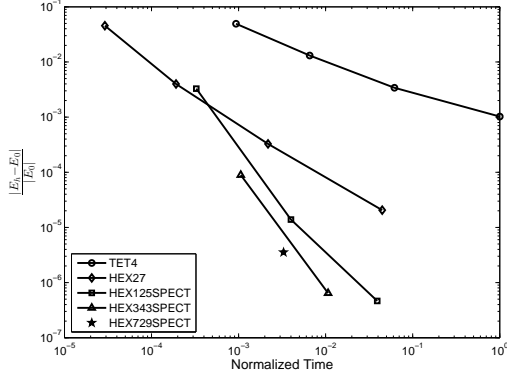
Figure 4: Computational efficiency of various orders of finite-element approximations. Case study: Barium $2 \times 2 \times 2$ BCC cluster. (Motamarri et al., 2013)
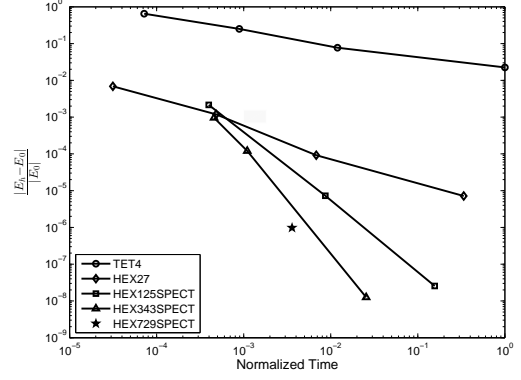
Figure 5: Computational efficiency of various orders of finite-element approximations. Case study: Methane molecule. (Motamarri et al., 2013)

effort, we also developed computational techniques that enable large-scale Kohn-Sham DFT calculations. The ground-state properties in Kohn-Sham DFT are given by the solution of Kohn-Sham equations:

$$\mathcal{H}\psi_i = \epsilon_i \psi_i, \tag{2}$$

where

$$\mathcal{H} = \left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\rho, \boldsymbol{R}) \right) \tag{3}$$

is a Hermitian operator with eigenvalues ϵ_i, and the corresponding orthonormal eigenfunctions ψ_i for $i = 1, 2, \cdots, N$ denote the canonical wavefunctions. The electron density in terms of the canonical wavefunctions is given by

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{x})|^2 \,, \tag{4}$$

and the effective single-electron potential $(V_{\text{eff}}(\rho, \boldsymbol{R}))$ with nuclear positions denoted by $\boldsymbol{R}$ in (3) is given by

$$V_{\text{eff}}(\rho, \boldsymbol{R}) = V_{ext}(\boldsymbol{R}) + V_H(\rho) + V_{xc}(\rho). \tag{5}$$

In the above, V_{ext}, $V_H(\rho)$, and $V_{xc}(\rho)$ denote the potentials associated with E_{ext}, E_H and E_{xc}. Fourier space calculations have been popular for Kohn-Sham DFT calculations as the computation of the electrostatic potentials, which are extended in real-space, can be conveniently computed using Fourier transforms. However, a Fourier-space formulation introduces periodicity restrictions which severely limits the study of defects in materials.

In the present work, building on the real-space formulation developed for orbital-free DFT, we implemented a real-space formulation for the Kohn-Sham equations. Furthermore, we used the finite-element discretization of the formulation which enables the consideration of complex boundary conditions, also provides the flexibility to use an adaptive basis set. Building on the numerical analysis conducted in orbital-free DFT, we computed the rates of convergence for higher-order finite-elements for both pseudopotential as well as all-electron
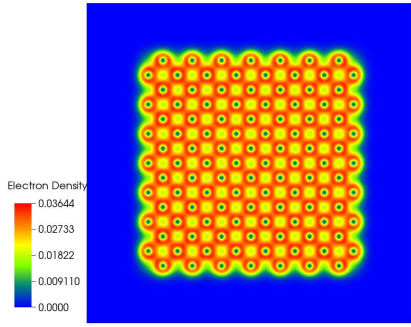
Figure 6: Electron density contours of $7 \times 7 \times 7$ FCC aluminium cluster. (Motamarri et al., 2013)
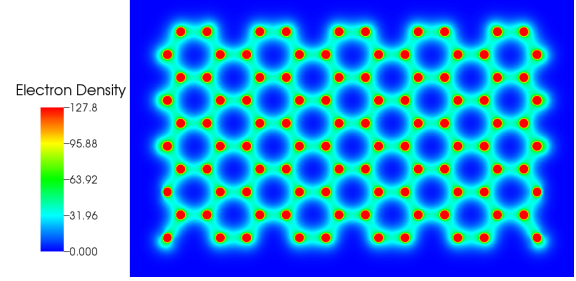

Figure 7: Electron density contours of 100 atoms graphene sheet. (Motamarri et al., 2013)

calculations. Further, we also estimated the computational efficiency afforded by higher-order finite-elements. As shown in figures 4 and 5, for chemical accuracies commensurate with chemical accuracy, higher-order finite-elements provide significant computational savings in comparison to linear finite-element discertizations. Using higher-order finite-element discretizations and Chebyshev acceleration techniques to efficiently compute the occupied eigenspace, we have demonstrated large-scale electronic structure calculations for both pseudopotentials and all-electrons—for instance a $7 \times 7 \times 7$ FCC cluster containing 1688 atoms (pseudopotential calculation) and a graphene sheet containing 100 atoms (all-electron).

Computations on reactive nanofilms: Building on our developments in Kohn-Sham DFT, we incorporated non-local Troullier-Martins pseudopotential in the Kleinman Bylander form and conducted studies on Ni-Al bi-layers. In particular, we computed the excess energy in the bi-layer system as a function of the bi-layer thickness. This excess energy is computed as the difference in the energy of the Ni-Al bilayer system and the energy of bulk Al and Ni atoms with similar composition. Figure 8 shows the excess energies of a Ni-Al bilayers along (100) as a function of the bi-layer thickness. For small bi-layer thickness this excess energy is negative suggesting that the decrease in the energy due to bonding at the interface is greater than the increase in the energy due to lattice mismatch. However, with increasing bilayer thickness this excess energy increases proportionally with the bi-layer thickness, which is a result of the elastic energy from the lattice mismatch. Beyond a particular bilayer thickness it becomes energetically favorable to nucleate threading dislocations. In our future investigations we seek to compute the critical bilayer thickness at which the dislocations nucleate.

3   Development of Software:

In collaboration with a team of scientists at Army Research Labs, which includes Mr. Kenneth Leiter, Mr. Joshua Crone, Dr. Michael Scott, Dr. Jaroslaw Knap and Dr. Peter Chung, we have committed significant time and effort towards developing a software out of the computational techniques developed over the course of this project. This software is being jointly developed by the group members of the PI and the team from ARL, and
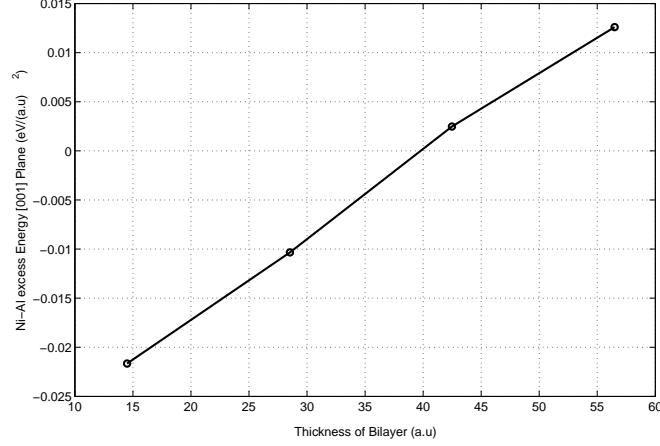
Figure 8: Excess energy as a function of bi-layer thickness of Ni-Al bi-layers.

is maintained in a repository. There is an active ongoing collaboration with ARL in the development of this software with weekly conference calls and annual visits by PI and his students to ARL.

4 Publications supported by ARO

1. Motamarri, P., Nowak, M.R., Leiter, K., Knap, J., Gavini, V., Higher-order adaptive finite-element discretization of Kohn-Sham density functional theory. *J. Comp. Phys.* (revision submitted, 2012).

2. Motamarri, P., Iyer, M., Knap, J., Gavini, V., Higher-order adaptive finite-element discretization of orbital-free density functional theory. *J. Comp. Phys.* **231** 6596-6621 (2012).

3. Gavini, V., Liu, L., A homogenization analysis of the field theoretical approach to the quasi-continuum method. *J. Mech. Phys. Solids* 59 1536-1551 (2011).

4. Radhakrishnan, B.G., Gavini, V., Effect of cell size on the energetics of vacancies in aluminum studied via orbital-free density functional theory. *Phys. Rev. B* **82**, 094117 (2010).

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Gavini, V., Bhattacharya, K., Ortiz, M., Quasi-continuum orbital-free density-functional theory: A route to multi-million atom non-periodic DFT calculation. *J. Mech. Phys. Solids* **55**, 697-718 (2007).

Motamarri, P., Nowak, M.R., Leiter, K., Knap, J., Gavini, V., Higher-order adaptive finite-element formulation of Kohn-Sham density functional theory. *J. Comp. Phys.* (revision submitted, 2012).

Motamarri, P., Iyer, M., Leiter, K., Knap, J., Gavini, V., Higher-order adaptive finite-element formulation of Orbital-free density functional theory. *J. Comp. Phys.* **231** 6596-6621 (2012).

Radhakrishnan, B.G., Gavini, V., Effect of cell size on the energetics of vacancies in aluminum studied via orbital-free density functional theory. *Phys. Rev. B* **82**, 094117 (2010).

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Zhou, B., Wang, Y.A., Carter, E.A., Transferable local pseudopotentials derived via inversion of the Kohn-Sham equations in a bulk environment *Phys. Rev. B* **69**, 125109 (2004).